Tetrahedron Letters No. 52, pp 4927 - 4930, 1971. Pergamon Press. Printed in Great Britain.

THE CORRECTED MCLACHLAN METHOD FOR RADICAL CATIONS: EVEN NON-ALTERNANT HYDROCARBONS.

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(Received in UK 26 October 1971; accepted for publication 24 November 1971)

ABSTRACT: An error in the application of the McLachlan method to radical cations is analysed in brief, and corrected. The corrected results are presented for a range of even non-alternant hydrocarbons; they differ significantly from those obtained by the incorrect method.

Attention has recently been drawn to the spurious disparity between the calculated π-electron spin densities of the anion and cation radicals of styrene[1,2]. This disparity arises when the anion or neutral radical formalism of McLachlan[3] is carried over to cation radicals without the appropriate analysis. Detailed and preliminary[2,4] accounts of this analysis are now available.

The expression hitherto in general use for calculating the π-electron distribution in all types of radicals[3] (ΔA method) is

$$\rho = |\psi_0^H|^2 + \sum_1^n \{ |\psi_i^P|^2 - |\psi_i^H|^2 \} \qquad \ldots 1$$

where ψ_0^H is the unperturbed orbital containing the odd α-electron, the ψ_i^H are the unperturbed orbitals containing the n β-electrons, and the ψ_i^P the perturbed orbitals containing the n exchange perturbed α-electrons. Although equation 1 is applicable to anion and neutral radicals, we have recently[2] shown that the correct expression for all conjugated cation radicals is

$$\rho = |\psi_0^P|^2 + \sum_1^{n-1} \{ |\psi_i^P|^2 - |\psi_i^H|^2 \} \qquad \ldots 2$$

Thus systems in which an electron pair has been separated in order to generate a radical ion require the placement of the odd α-electron into a perturbed rather than an unperturbed orbital. If this is not done, the pairing theorem of even alternant molecules is violated[2,4].

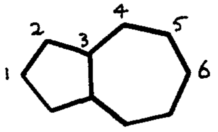
The perturbed orbitals can be obtained if the original Hückel parameters, $\alpha_r(0)$ of atom r, are altered by the appropriate Hückel spin density $\rho_r(0)$ to give (the $\Delta\alpha$ method)

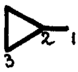
$$\alpha_r(1) = \alpha_r(0) + 2\lambda\rho_r(0) \qquad \ldots 3$$

where $\lambda \doteqdot 1.0$—1.2[3]. In addition the Hückel bonding parameters, $\beta_{rs}(0)$ can be altered concurrently (the $\Delta\beta$ method)[2]. Alternatively, use can be made of the atom-atom polarisability matrix (the POL method) as given by McLachlan[3] ,where the π'_{rs} ($\equiv \pi'_{rr,ss}$) are the dimensionless polarisabilities as defined and tabulated elsewhere[5].

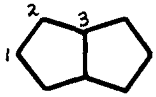
$$\rho_r(1) = \rho_r(0) - \lambda\sum_s \pi'_{rs}\rho_s(0) \qquad \ldots 4$$

The prime does not imply omission of r from the sum over s. An additional correction utilises atom-bond corrections for bonds involving the atom in question (the POL2 method) [2]. Available tabulations of orbitals and polarisabilities for a range of conjugated molecules [5] make it possible to apply the POL and POL2 methods to these molecules without recourse to computation. It has been recently shown[4] that an incorrectly defined polarisability leads to violation of the pairing theorem. We emphasise that the use of equation 4 does not lead to violation of either the pairing theorem or first order perturbation theory if the neutral molecule polarisabilities are always used. In fact we have used the latter for all types of conjugated radical ions [1,2]. Although it is possible to define a number of "perturbed polarisabilities" which do not violate the pairing

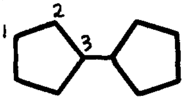
	Atom	$\Delta\alpha$	$\Delta\beta$	POL	POL2	ΔA Incorrect
 	1	-0.089	-0.078	-0.089	-0.089	-0.089
	2	0.385	0.366	0.393	0.387	0.400
	3	0.042	0.047	0.038	0.040	0.083 *
	4	0.006	0.010	0.007	0.009	-0.029 **
	5	0.130	0.136	0.126	0.126	0.108
	6	-0.037	-0.040	-0.037	-0.038	-0.037



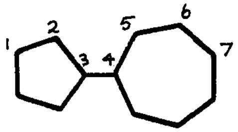
0.810
-0.033**
0.111



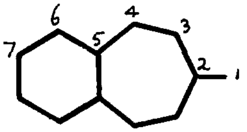
0.335
-0.037
0.240



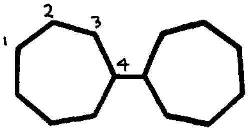
0.041
0.220
-0.022



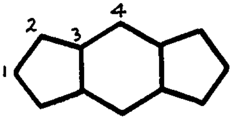
0.217
-0.023**
0.352*
-0.028
0.105*
-0.015*
0.054*



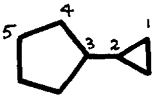
ΔA $\Delta\alpha$
0.631; 0.650
-0.017;-0.050*
0.070; 0.108
0.089; 0.033*
0.017; 0.040*
0.009;-0.003**
0.007; 0.022*



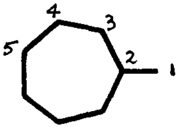
0.064
0.104
0.020
0.124



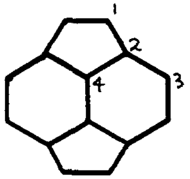
0.234 *
0.059 **
0.069 *
-0.027 *



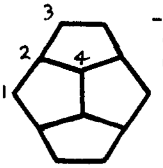
-0.015 *
-0.007
-0.095 *
0.454 *
0.112 **



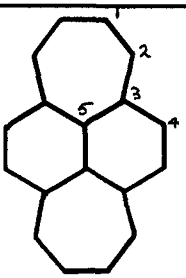
0.686
-0.066
0.129
-0.001 **
0.062



0.146
0.043
0.009
0.104



0.395*
-0.026*
0.020**
0.118



0.064
0.063
0.067
0.065
-0.018

Topology, labelling and corrected McLachlan π-electron spin densities of some even non-alternants, using $\lambda = 1.00$.

theorem, their use contravenes the first order perturbation theory[3] and leads to disagreement with the $\Delta\alpha$ method[2]. The error introduced when the perturbed orbitals are incorrectly used in the study of radical cations will only be small when the unperturbed HBO and perturbed HBO are similar. Fortuitously, the use of $\lambda = 1.2$ in the styrene cation radical calculations produces a perturbed HBO of different symmetry to that of the unperturbed HBO. The resulting large and spurious disparities between the anion and cation radicals, when equation 1 is used, first drew our attention to the presence of an error in the ΔA method[1].

The details of the corrected McLachlan results for fulvene and acepleiadylene have already been presented[2]. To demonstrate that the spin densities evaluated by the methods described are in fair agreement, we give all our results for azulene: for comparison we also include the incorrect results. For other molecules we give only the results from the $\Delta\alpha$ method. A single asterisk will denote a correction in magnitude $>50\%$, and a double asterisk will denote that an error in sign was given by the incorrect method.

References

1. C.L.Honeybourne. Chem.Phys.Letts., 8, 493 (1971)
2. C.L.Honeybourne. Mol.Phys., 21, 1057 (1971)
3. A.D.McLachlan. Mol.Phys., 3, 233 (1960)
4. J.C.Bickerton and R.E.Moss. Mol.Phys., 21, 341 (1971).
5. C.A.Coulson and A.Streitwieser. A Dictionary of π-electron Calculations. (Pergamon, London, 1965); supplement 1970.